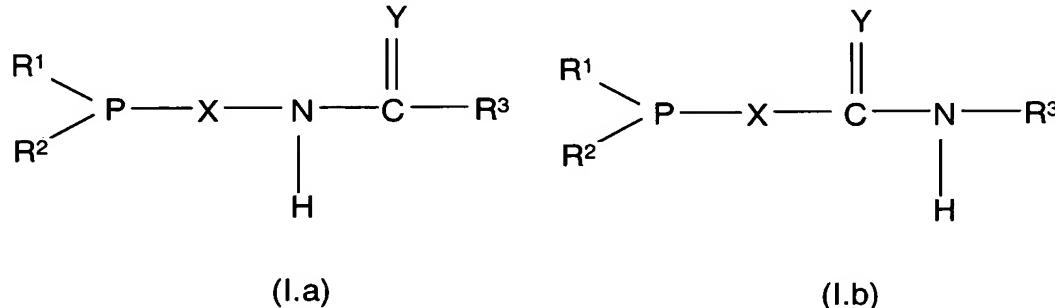


We claim:

1. A process for hydroformylating compounds which contain at least one ethylenically unsaturated double bond by reacting with carbon monoxide and hydrogen in the presence of a catalyst comprising at least one complex of a metal of transition group VIII of the Periodic Table of the Elements with ligands which each have a phosphorus group and at least one functional group which is capable of forming intermolecular noncovalent bonds, wherein the complex has ligands which are dimerized via intermolecular noncovalent bonds and wherein the distance between the phosphorus atoms of the dimerized ligands is at most 5 Å.
2. A process as claimed in claim 1, wherein the distance between the phosphorus atoms of the dimerized ligands is in the range from 2.5 to 4.5 Å, preferably from 3.5 to 4.2 Å, especially from 3.6 to 4.1 Å.
3. A process as claimed in either of claims 1 or 2, wherein the functional groups which are capable of forming intermolecular noncovalent bonds are selected from hydroxyl, primary, secondary and tertiary amino, thiol, keto, thioketone, imine, carboxylic ester, carboxamide, amidine, urethane, urea, sulfoxide, sulfoximine, sulfonamide and sulfonic ester groups.
4. A process as claimed in any of the preceding claims, wherein the functional groups which are capable of forming intermolecular noncovalent bonds are selected from groups which are capable of tautomerizing.
5. A process as claimed in any of the preceding claims, wherein the ligands include at least one structural element of the general formulae I.a or I.b



30

or tautomers thereof where

35 R^1 and R^2 are each independently alkyl, alkoxy, cycloalkyl, cycloalkoxy, heterocycloalkyl, heterocycloalkoxy, aryl, aryloxy, hetaryl or hetaryloxy,

R^3 is hydrogen or is as defined for R^1 and R^2 ,

X is a bivalent bridging group having from 1 to 5 bridging atoms between the flanking bonds,

5 Y is O, S or NR⁴, where R⁴ is hydrogen, alkyl, cycloalkyl, heterocycloalkyl, aryl or hetaryl,

and two or more than two of the X radicals and R¹ to R⁴ together with the structural element of the formula I.a or I.b to which they are bonded may be a
10 mono- or polycyclic compound.

6. A process as claimed in claim 5, wherein R¹ and R² in the ligands I.a or I.b, together with the phosphorus atom to which they are bonded, are each a 5- to
15 8-membered heterocycle which may optionally additionally be singly, doubly or triply fused with cycloalkyl, heterocycloalkyl, aryl or hetaryl, and the heterocycle and, where present, the fused groups may each independently bear one, two, three or four substituents which are selected from alkyl, cycloalkyl, heterocycloalkyl, aryl, hetaryl, COOR^c, COO⁻M⁺, SO₃R^c, SO₃⁻M⁺, PO₃(R^c)(R^d), (PO₃)²⁻(M⁺)₂, NE⁴E⁵, (NE⁴E⁵E⁶)⁺X⁻, OR^e, SR^e, (CHR^fCH₂O)_yR^e, (CH₂NE⁴)_yR^e,
20 (CH₂CH₂NE⁴)_yR^e, halogen, nitro, acyl and cyano, where

R^c and R^d are each identical or different radicals selected from alkyl, cycloalkyl, aryl and hetaryl,

25 R^e, E⁴, E⁵, E⁶ are each identical or different radicals selected from hydrogen, alkyl, cycloalkyl, acyl, aryl and hetaryl,

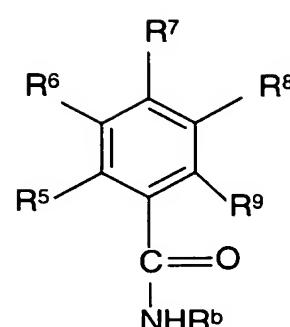
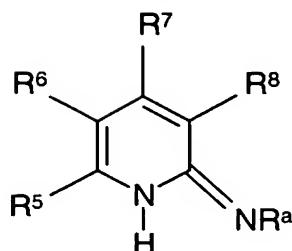
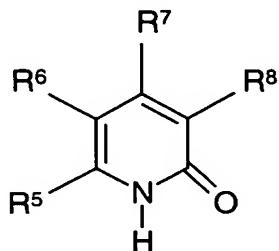
R^f is hydrogen, methyl or ethyl,

30 M⁺ is one cation equivalent,

X⁻ is one anion equivalent and

y is an integer from 1 to 240.

35 7. A process as claimed in any of the preceding claims, wherein the ligands are selected from compounds of the general formulae I.1 to I.3



and the tautomers thereof where

5 one of the R⁵ to R⁹ radicals is a group of the formula
—W'—PR¹R² where

10 W' is a single bond, a heteroatom, a heteroatom-containing group or a bivalent bridging group having from 1 to 4 bridging atoms between the flanking bonds,

R¹ and R² are each as defined in either of claims 4 or 5,

15 the R⁵ to R⁹ radicals which are not —W'—PR¹R² are each independently hydrogen, alkyl, cycloalkyl, heterocycloalkyl, aryl, hetaryl, WCOOR^o, WCOO⁻M⁺, W(SO₃)R^o, W(SO₃)M⁺, WPO₃(R^o)(R^p), W(PO₃)²⁻(M⁺)₂, WNE¹E², W(NE¹E²E³)⁺X⁻, WOR^q, WSR^q, (CHR^rCH₂O)_xR^q, (CH₂NE¹)_xR^q, (CH₂CH₂NE¹)_xR^q, halogen, nitro, acyl or cyano,

20 where

W is a single bond, a heteroatom, a heteroatom-containing group or a bivalent bridging group having from 1 to 20 bridging atoms,

25 R^o and R^p are each identical or different radicals selected from alkyl, cycloalkyl, aryl and hetaryl,

R^q, E¹, E², E³ are each identical or different radicals selected from hydrogen, alkyl, cycloalkyl, acyl, aryl and hetaryl,

30 R^r is hydrogen, methyl or ethyl,

M⁺ is one cation equivalent,

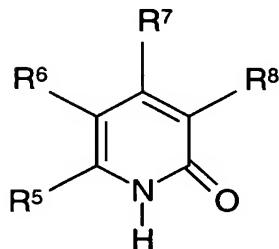
X⁻ is one anion equivalent and

x is an integer from 1 to 240,

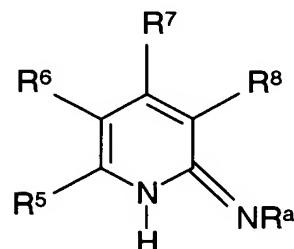
5 and in each case two adjacent R⁵, R⁶, R⁷, R⁸ and R⁹ radicals, together with the ring carbon atoms to which they are bonded, may also be a fused ring system having 1, 2 or 3 further rings, and

10 R^a and R^b are each hydrogen, alkyl, acyl, cycloalkyl, heterocycloalkyl, aryl or hetaryl.

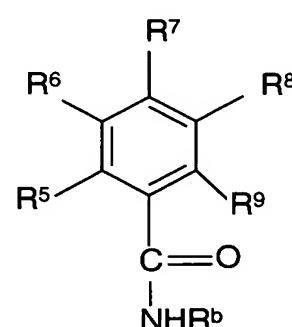
8. A process for hydroformylating compounds which contain at least one ethylenically unsaturated double bond by reacting with carbon monoxide and hydrogen in the presence of a catalyst comprising at least one complex of a 15 metal of transition group VIII of the Periodic Table of the Elements with ligands which are selected from compounds of the general formulae I.1 to I.3



(I.1)



(I.2)



(I.3)

20 and the tautomers thereof where

one of the R⁵ to R⁹ radicals is a group of the formula
—W'—PR¹R² where

25 W' is a single bond, a heteroatom, a heteroatom-containing group or a bivalent bridging group having from 1 to 4 bridging atoms between the flanking bonds,

R¹ and R² are each as defined in either of claims 4 or 5,

30 the R⁵ to R⁹ radicals which are not —W'—PR¹R² are each independently hydrogen, alkyl, cycloalkyl, heterocycloalkyl, aryl, hetaryl, WCOOR^o, WCOOM⁺, W(SO₃)R^o, W(SO₃)M⁺, WPO₃(R^o)(R^p), W(PO₃)²⁻(M⁺)₂, WNE¹E²,

W(NE¹E²E³)⁺X⁻, WOR^q, WSR^q, (CHR^rCH₂O)_xR^q, (CH₂NE¹)_xR^q,
(CH₂CH₂NE¹)_xR^q, halogen, nitro, acyl or cyano,

where

5

W is a single bond, a heteroatom, a heteroatom-containing group or a bivalent bridging group having from 1 to 20 bridging atoms,

10

R^o and R^p are each identical or different radicals selected from alkyl, cycloalkyl, aryl and hetaryl,

15

R^q, E¹, E², E³ are each identical or different radicals selected from hydrogen, alkyl, cycloalkyl, acyl, aryl and hetaryl,

20

R^r is hydrogen, methyl or ethyl,

M⁺ is one cation equivalent,

X⁻ is one anion equivalent and

25

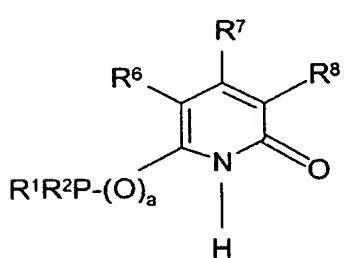
x is an integer from 1 to 240,

and in each case two adjacent R⁵, R⁶, R⁷, R⁸ and R⁹ radicals, together with the ring carbon atoms to which they are bonded, may also be a fused ring system having 1, 2 or 3 further rings, and

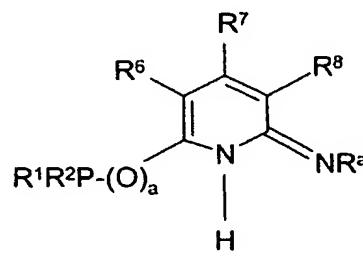
R^a and R^b are each hydrogen, alkyl, acyl, cycloalkyl, heterocycloalkyl, aryl or hetaryl.

30 9.

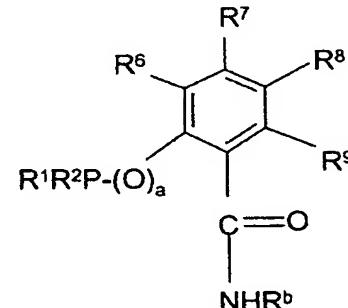
A process as claimed in either of claims 6 or 7, wherein the ligands are selected from compounds of the general formulae I.i to I.iii



(I.i)



(I.ii)



(I.iii)

and the tautomers thereof where

a is 0 or 1,

R¹ and R² are each as defined above,

5

R⁶ to R⁹ are each independently hydrogen, C₁-C₄-alkyl, C₁-C₄-alkoxy, acyl, aryl, heteroaryl, halogen, C₁-C₄-alkoxycarbonyl or carboxylate,

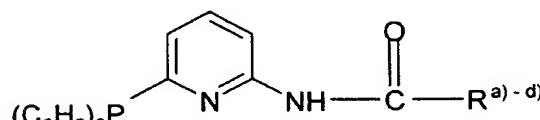
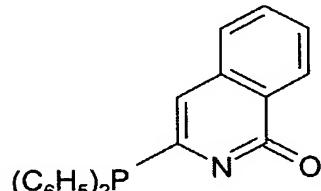
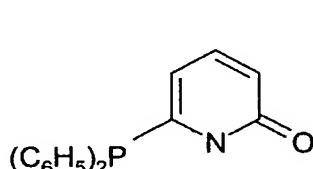
10

and in each case two adjacent R⁶, R⁷, R⁸ and R⁹ radicals, together with the ring carbon atoms to which they are bonded, may also be a fused ring system having 1, 2 or 3 further rings, and

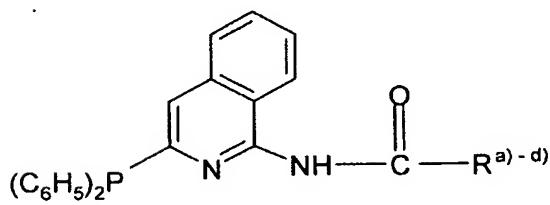
R^a and R^b are each hydrogen, alkyl, acyl, cycloalkyl or aryl.

15

10. A process as claimed in any of the preceding claims, wherein the ligands used comprise at least one compound of the formulae (1) to (4)



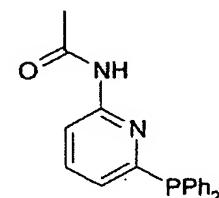
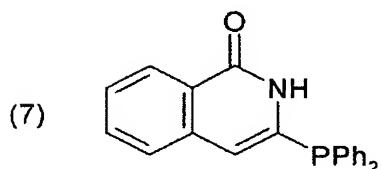
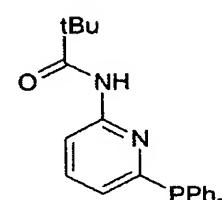
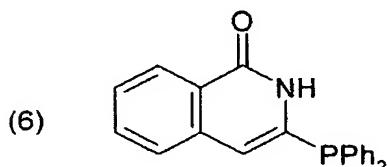
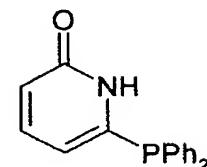
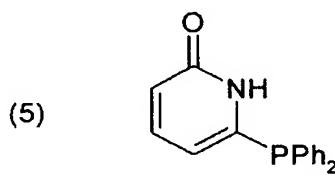
- a) CH₃
- b) C₂H₅
- c) iso-C₃H₇
- d) tert-C₄H₉



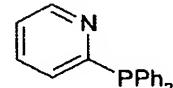
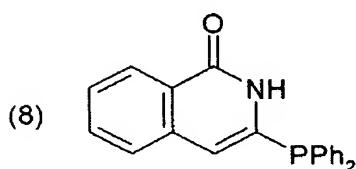
- a) CH₃
- b) C₂H₅
- c) iso-C₃H₇
- d) tert-C₄H₉

20

11. A process as claimed in any of the preceding claims, wherein the ligand used is one of the following ligands/ligand pairs (5) to (8):



5



12. A catalyst as defined in any of claims 1 to 11.

10 13. A catalyst as claimed in claim 12, wherein the metal is selected from cobalt, nickel, rhodium, ruthenium and iridium.

14. A process for preparing 2-propylheptanol, by

15 a) hydroformylating butene or a butene-containing C₄ hydrocarbon mixture in the presence of a catalyst as defined in either of claims 12 or 13 with carbon monoxide and hydrogen to obtain an n-valeraldehyde-containing hydroformylation product,

20 b) optionally subjecting the hydroformylation product to a separation to obtain an n-valeraldehyde-enriched fraction,

- c) subjecting the hydroformylation product obtained in step a) or the n-valeraldehyde-enriched fraction obtained in step b) to an aldol condensation,
- 5 d) catalytically hydrogenating the products of the aldol condensation with hydrogen to give alcohols, and
- e) optionally subjecting the hydrogenation products to a separation to obtain a 2-propylheptanol-enriched fraction.

10 15. A process for preparing an ester mixture, wherein an alcohol mixture obtainable by a process as defined in claim 14 is reacted with at least one acid which is selected from aliphatic di- and tricarboxylic acids, aromatic mono-, di- and tricarboxylic acids, phosphoric acid and derivatives and mixtures thereof.

15 16. The use of a catalyst as defined in either of claims 12 or 13 for hydroformylating, carbonylating or hydrogenating.